TRANSMITTAL LETTER TO THE UNITED STATES

Attorney's Docket Number 2014 5725.0545

DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

International Filing Date

DOT/	DDOO	1015	0.1	

Title of Invention:

OXIDATION DYEING COMPOSITION FOR KERATINOUS FIBRES AND DYBING METHOD USING SAME

Applicant(s) For DO/EO/US:

International Application. No.

the		cant herewith submits to the United States Designated/Elected Office (Do/EO/US) ring items and other information:
1.	[X]	This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2.	[]	This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3.	[]	This express request to begin national examination procedures (35 U.S.C. $371(f)$) at any time rather than delay examination until the expiration of the applicable
•		time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4.	[]	A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5.	[X]	A copy of the International Application as filed (35 U.S.C. 371(c)(2))
		a. [] is transmitted herewith (required only if not transmitted by the International Bureau).
per capital		b. [X] has been transmitted by the International Bureau.
		c. [] is not required, as the application was filed in the United States Receiving Office (RO/US).
5.05	[X]	A translation of the International Application into English (35 U.S.C. 371(c)(2)
5. Ø	[X]	Amendments to the claims of the International Application under PCT Article 19
SEE APA		(35 U.S.C. 371(c)(3)).
H L		 a. [] are transmitted herewith (required only if not transmitted by the International Bureau).
W		b. [] have been transmitted by the International Bureau.
N		c. [] have not been made; however, the time limit for making such amendments has NOT expired.
N		d. [X] have not been made and will not be made.
3.0	[]	A translation of the amendments to the claims under PCT Article 19
C		(35 U.S.C. 371(c)(3)).
9.	[]	An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10.	[]	A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
tem	s 11.	to 16. below concern other document(s) or information included:
.1.		An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
. 2.	F 1	An assignment document for recording A separate cover sheet in compliance with

- 37 CFR 3.28 and 3.31 is included.
- A FIRST preliminary amendment.
 - [] A SECOND or SUBSEQUENT preliminary amendment. [] A substitute specification.
- 15. [] A change of power of attorney and/or address letter.

14.

- Other items or information:
 - a. [] Verified Small Entity Statement.
 - [] Copy of Notification of Missing Requirements.

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	U7/4027U4	PCT/FR99/01291	١

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17. [X]	The following fees are submitted:			l CA	LCULATIONS
	Basic National Fee (37 CFR 1.492(a)(1)-	(5)):			
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	d to USPTO (37 CFR 1.445(a)(2))		760.00	i	
	er international preliminary examination			i	
	CFR 1.482) nor international search fee			i	
(3.	CFR 1.445(a)(2)) paid to USPTO	\$	970.00	İ	
Inter	national preliminary examination fee pai	d to USPTO		İ	
(31	CFR 1.482) and all claims satisfied pro	visions		İ	
of	PCT Article 33(1)-(4)	\$	96.00	<u>i</u>	
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The Commissioner is hereby authorized to charge any other fees due under 37 C.F.R. $\S1.16$ or $\S1.17$ during the pendency of this application to our Deposit Account No, 06-0916.

SEND ALL CORRESPONDENCE TO: Finnegan, Henderson, Farabow Garrett & Dunner, L.L.P. 1300 I Street, N.W. Washington, D.C. 20005-3315 EFC/FPD/rqm

Ernest F. Chapman Reg. No. 25,961

Submitted: February 18, 2000

09 / 485904 428 Rec'd PCT/PTO 18 FEB 2000

PATENT Attorney Docket No. 5725.0545

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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	In re Application of:)	National Stage Application of PCT Application No.
No. of Street, or other Persons	Marie-Pascale AUDOUSSET)	PCT/FR99/01291
OF REAL PROPERTY.	Serial No.: not yet assigned)	Group Art Unit: not yet assigned
-	Filed: February 18, 2000)	Examiner: not yet assigned
	For: OXIDATION DYEING COMPOS DYEING METHOD USING SAM		FOR KERATINOUS FIBRES AND
	Assistant Commissioner for Patents Washington, D.C. 20231		
	Sir:		

PRELIMINARY AMENDMENT

Prior to initial examination, please amend the application as follows:

IN THE CLAIMS:

Please cancel claims 1-15 without prejudice to or disclaimer of the subject matter contained therein

Please add new claims 16-40 as follows:

- --16. A composition for the oxidation dyeing of keratinous fibers comprising:
- at least one first oxidation base chosen from pyrazolo(1,5-a)pyrimidines of formula (I) and acid or base addition salts thereof:

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L. L. P. 1300 I STREET, N. W. WASHINGTON, D. C. 20005

$$(X)_{i} = \begin{bmatrix} N & 3 & \\ 5 & N - N \end{bmatrix}^{2} = \begin{bmatrix} NR_{1}R_{2}I_{p} & \\ INR_{3}R_{4}I_{q} & \end{bmatrix}$$
 (I)

in which:

 $-R_1,\,R_2,\,R_3\,\text{and}\,R_4,\,\text{which are identical or different, are chosen from a hydrogen atom; a $(C_1\text{-}C_4)$alkyl radical; an aryl radical; a hydroxy($C_1\text{-}C_4$)alkyl radical; a polyhydroxy($C_2\text{-}C_4$)alkyl radical; a $(C_1\text{-}C_4)$alkyl radical; an amino($C_1\text{-}C_4$)alkyl radical wherein said amine is optionally protected by an acetyl, an amido, or a sulphonyl group; a $(C_1\text{-}C_4)$alkylamino($C_1\text{-}C_4$)alkyl radical; a $di((C_1\text{-}C_4)$alkyl)$amino($C_1\text{-}C_4$)alkyl radical wherein said dialkyls optionally form a 5-or 6-membered aliphatic or heterocyclic ring; a $hydroxy($C_1\text{-}C_4$)alkylamino($C_1\text{-}C_4$)alkyl radical; and a $di(hydroxy($C_1\text{-}C_4$)alkyl)$amino($C_1\text{-}C_4$)alkyl radical;$

- the X radicals, which are identical or different, are chosen from a hydrogen atom; a (C_1-C_4) alkyl radical; an aryl radical; a hydroxy (C_1-C_4) alkyl radical; a polyhydroxy (C_2-C_4) alkyl radical; an amino (C_1-C_4) alkyl radical; a $((C_1-C_4)$ alkylamino (C_1-C_4) alkyl radical; a di $((C_1-C_4)$ alkyl)amino (C_1-C_4) alkyl radical

wherein said dialkyls optionally form a 5- or 6-membered aliphatic or heterocyclic ring; a hydroxy(C_1 - C_4)alkylamino(C_1 - C_4)alkyl radical; a di((hydroxy(C_1 - C_4)alkyl)amino(C_1 - C_4)alkyl radical; a namino radical; a (C_1 - C_4)alkylamino radical; a halogen atom; a carboxylic acid group; and a sulphonic acid group;

- i is 0, 1, 2 and 3;
- p is 0 or 1;
- q is 0 or 1;
- n is 0 or 1;with the proviso that:
- -(i) the sum p + q is other than 0;
- -(ii) when p + q is equal to 2, then n is 0 and the NR_1R_2 and NR_3R_4 groups occupy the (2,3), (5,6), (6,7), (3,5) or (3,7) positions;
- -(iii) when p + q is equal to 1, then n is 1 and either the NR_1R_2 or the NR_3R_4 group and the OH group occupy the (2,3), (5,6), (6,7), (3,5) or (3,7) positions;
- at least one second oxidation base chosen from N,N-bis(β-hydroxyethyl)- paraphenylenediamine and its acid addition salts; and
- at least one coupler chosen from meta-phenylenediamines and meta-aminophenols of formula (II) and acid addition salts thereof:

$$\begin{array}{c|c} & \text{OH} & \\ & &$$

in which:

- R_s and R_s , which are identical or different, are chosen from a hydrogen atom, a halogen atom, or a (C_1-C_4) alkyl, monohydroxy (C_1-C_4) alkyl, polyhydroxy (C_2-C_4) alkoxy, monohydroxy (C_1-C_4) alkoxy or polyhydroxy (C_2-C_4) alkoxy radical;
- R₆ is chosen from a hydrogen atom and a (C₁-C₄)alkyl, monohydroxy(C₁-C₄)alkyl, polyhydroxy(C₂-C₄)alkyl or an amino(C₁-C₄)alkyl radical;
- R₇ is chosen from a hydrogen atom, a (C₁-C₄)alkyl or (C₁-C₄)alkoxy radical and a halogen atom chosen from chlorine, bromine or fluorine;
 - it being understood that, when $R_{\rm 5}$ represents a chlorine atom and when $R_{\rm 6}$ and $R_{\rm 7}$ simultaneously represent a hydrogen atom, then $R_{\rm 8}$ is other than a methyl radical.
- The composition according to claim 16, wherein the keratinous fibers are human keratinous fibers.

- The composition according to claim 17, wherein the human keratinous fibres are hair.
- The composition according to claim 16, further comprising a medium appropriate for dyeing.
- $20. \quad \text{The composition according to claim 16, wherein when R_5 or R_8 is a} \\ \text{halogen atom, said halogen atom is chosen from chlorine, bromine, iodine and fluorine.}$
- 21. The composition according to claim 16, wherein the pyrazolo(1,5-a)pyrimidines of formula (I) are chosen from:
- pyrazolo(1,5-a)pyrimidine-3,7-diamine;
- 2-methylpyrazolo(1,5-a)pyrimidine-3,7-diamine;
- 2,5-dimethylpyrazolo(1,5-a)pyrimidine-3,7-diamine;
- pyrazolo(1,5-a)pyrimidine-3,5-diamine;
- 2,7-dimethylpyrazolo(1,5-a)pyrimidine-3,5-diamine;
- 3-aminopyrazolo(1,5-a)pyrimidin-7-ol;
- 3-amino-5-methylpyrazolo(1,5-a)pyrimidin-7-ol;
- 3-aminopyrazolo(1,5-a)pyrimidin-5-ol;
- 2-(3-aminopyrazolo(1,5-a)pyrimidin-7-ylamino)ethanol;
- 3-amino-7-(β-hydroxyethylamino)-5-methylpyrazolo(1,5-a)pyrimidine;
- 2-(7-aminopyrazolo(1,5-a)pyrimidin-3-ylamino)ethanol;

- 2-((3-aminopyrazolo(1,5-a)pyrimidin-7-yl)(2-hydroxyethyl)amino)ethanol;
- 2-((7-aminopyrazolo(1,5-a)pyrimidin-3-yl)(2-hydroxyethyl)amino)ethanol;
- 5,6-dimethylpyrazolo(1,5-a)pyrimidine-3,7-diamine;
- 2,6-dimethylpyrazolo(1,5-a)pyrimidine-3,7-diamine;
- 2,5,N-7,N-7-tetramethylpyrazolo(1,5-a)pyrimidine-3,7-diamine;

and acid or base addition salts thereof.

22. The composition according to claim 16, wherein the metaphenylenediamines are chosen from the compounds of formula (III) and acid addition salts thereof:

$$\begin{array}{c|c} & \text{NH}_2 \\ \hline R_{12} & \\ \hline R_{11} & \text{NHR}_g \end{array} (III)$$

in which:

- R₉ is chosen from a hydrogen atom, a (C₁-C₄)alkyl radical, a monohydroxy(C₁-C₄)alkyl radical and a polyhydroxy(C₂-C₄)alkyl radical;

- R_{10} and R_{11} , which are identical or different, are chosen from a hydrogen atom, a (C_1-C_4) alkyl radical, a monohydroxy (C_1-C_4) alkoxy radical, and a polyhydroxy (C_2-C_4) alkoxy radical;
- R_{12} is chosen from a hydrogen atom, a (C_1-C_4) alkoxy radical, an amino (C_1-C_4) alkoxy radical, a monohydroxy (C_1-C_4) alkoxy radical, a polyhydroxy (C_2-C_4) alkoxy radical, and a 2,4-diaminophenoxyalkoxy radical.
- 23. The composition according to claim 22, wherein the meta-phenylenediamines are chosen from meta-phenylenediamine, 3,5-diamino-1-ethyl-2-methoxybenzene, 3,5-diamino-2-methoxy-1-methylbenzene, 2,4-diamino-1-ethoxybenzene, 1,3-bis(2,4-diaminophenoxy)propane, bis(2,4-diaminophenoxy)methane, 1-(β-aminoethyloxy)-2,4-diaminobenzene, 2-amino-1-(β-hydroxyethyloxy)-4-(methylamino)benzene, 2,4-diamino-1-ethoxy-5-methylbenzene, 2,4-diamino-5-(β-hydroxyethyloxy)-1-methylbenzene, 2,4-diamino-1-(β-hydroxyethyloxy)benzene, 2-amino-4-N-(β-hydroxyethyl)amino-1-methoxybenzene and acid addition salts thereof.
- 24. The composition according to claim 16, wherein the meta-aminophenols are chosen from meta-aminophenol, 5-amino-2-methoxyphenol, 5-amino-2-fb-hydroxyethyloxy)phenol, 5-amino-2-methylphenol, 5-N-(β-hydroxyethyl)amino-2-methylphenol, 5-N-(β-hydroxyethyl)amino-4-methoxy-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-methoxy-2-meth

- 2,4-dimethoxyphenol, 5-(γ-hydroxypropylamino)-2-methylphenol, 3-amino-6-chlorophenol, 3-amino-6-chlorophenol, 3-(β-aminoethyl)amino-6-chlorophenol, 3-(β-hydroxyethyl)amino-6-chlorophenol and acid addition salts thereof.
- 25. The composition according to claim 16, wherein said at least one first oxidation base is present in the composition in an amount ranging from 0.0005 to 12% by weight relative to the total weight of the composition.
- 26. The composition according to claim 25, wherein said at least one first oxidation base is present in an amount ranging from 0.005 to 6% by weight relative to the total weight of the composition.
- 27. The composition according to claim 16, wherein said at least one second oxidation base is present in the composition in an amount ranging from 0.0005 to 12% by weight relative to the total weight of the composition.
- 28. The composition according to claim 27, wherein said at least one second oxidation base is present in the composition in an amount ranging from 0.005 to 6% by weight relative to the total weight of the composition.
- 29. The composition according to claim 16, wherein said at least one coupler is present in the composition in an amount ranging from 0.0001 to 10% by weight relative to the total weight of the composition.

- 30. The composition according to claim 29, wherein said at least one coupler is present in the composition in an amount ranging from 0.005 to 5% by weight relative to the total weight of the composition.
- 31. The composition according to claim 16, wherein the acid addition salts are chosen from hydrochlorides, hydrobromides and sulphates and tartrates, lactates and acetates and wherein the base addition salts are chosen from those obtained with sodium hydroxide, potassium hydroxide, aqueous ammonia and amines.
- 32. A process for dyeing keratinous fibers comprising: applying to said keratinous fibers at least one dyeing composition comprising: at least one first oxidation base chosen from pyrazolo(1,5-a)pyrimidines of formula (I) and acid or base addition salts thereof:

$$(X)_{i} = \begin{bmatrix} N & 3 \\ N & N \end{bmatrix}^{2} = \begin{bmatrix} [NR_{1}R_{2}]_{p} \\ [NR_{3}R_{4}]_{q} \end{bmatrix}$$
 (I)

in which:

- R₁, R₂, R₃ and R₄, which are identical or different, are chosen from a hydrogen atom; a $(C_1\text{-}C_4)$ alkyl radical; an aryl radical; a hydroxy($C_1\text{-}C_4$)alkyl radical; a polyhydroxy($C_2\text{-}C_4$)alkyl radical; a $(C_1\text{-}C_4)$ alkoxy($C_1\text{-}C_4$)alkyl radical; an amino($C_1\text{-}C_4$)alkyl radical wherein said amine is optionally protected by an acetyl, an amido, or a sulphonyl group; a $(C_1\text{-}C_4)$ alkylamino($C_1\text{-}C_4$)alkyl radical; a di($(C_1\text{-}C_4)$ alkyl)amino($C_1\text{-}C_4$)alkyl radical wherein said dialkyls optionally form a 5-or 6-membered aliphatic or heterocyclic ring; a hydroxy($C_1\text{-}C_4$)alkylamino($C_1\text{-}C_4$)alkyl radical; and a di(hydroxy($C_1\text{-}C_4$)alkyl)amino($C_1\text{-}C_4$)alkyl radical;

- the X radicals, which are identical or different, are chosen from a hydrogen atom; a (C_1-C_4) alkyl radical; an aryl radical; a hydroxy(C_1-C_4)alkyl radical; a polyhydroxy(C_2-C_4)alkyl radical; an amino(C_1-C_4)alkyl radical; a (C_1-C_4) alkylamino(C_1-C_4)alkyl radical; a di((C_1-C_4) alkyl)amino(C_1-C_4)alkyl radical wherein said dialkyls optionally form a 5- or 6-membered aliphatic or heterocyclic ring; a hydroxy(C_1-C_4)alkylamino(C_1-C_4)alkyl radical; a di((hydroxy(C_1-C_4)alkyl)amino(C_1-C_4)alkyl radical; an amino radical; a (C_1-C_4) alkylamino radical; a di((C_1-C_4)alkyl)amino radical; a halogen atom; a carboxylic acid group; and a sulphonic acid group;

- i is 0, 1, 2 and 3;
- p is 0 or 1;

- q is 0 or 1;
- with the proviso that:

n is 0 or 1:

- -(iv) the sum p + q is other than 0;
- -(v) when p + q is equal to 2, then n is 0 and the NR_1R_2 and NR_3R_4 groups occupy the (2,3), (5,6), (6,7), (3,5) or (3,7) positions;
- -(vi) when p + q is equal to 1, then n is 1 and either the NR_1R_2 or the NR_3R_4 group and the OH group occupy the (2,3), (5,6), (6,7), (3,5) or (3,7) positions;
- at least one second oxidation base chosen from N,N-bis(β-hydroxyethyl)- paraphenylenediamine and its acid addition salts; and
- at least one coupler chosen from meta-phenylenediamines and meta-aminophenols of formula (II) and acid addition salts thereof:

$$\begin{array}{c} R_{8} \\ \hline \\ NHR_{6} \end{array} \qquad (II)$$

in which:

- R₅ and R₈, which are identical or different, are chosen from a hydrogen atom, a halogen atom, or a (C₁-C₄)alkyl, monohydroxy(C₁-C₄)alkyl, polyhydroxy(C₂-C₄)alkyl, (C₁-C₄)alkoxy, monohydroxy(C₁-C₄)alkoxy or polyhydroxy(C₂-C₄)alkoxy radical;
- R₆ is chosen from a hydrogen atom and a (C₁-C₄)alkyl, monohydroxy(C₁-C₄)alkyl, polyhydroxy(C₂-C₄)alkyl or an amino(C₁-C₄)alkyl radical;
- R₇ is chosen from a hydrogen atom, a (C₁-C₄)alkyl or (C₁-C₄)alkoxy radical and a halogen atom chosen from chlorine, bromine or fluorine;

it being understood that, when $R_{\rm s}$ represents a chlorine atom and when $R_{\rm s}$ and $R_{\rm 7}$ simultaneously represent a hydrogen atom, then $R_{\rm g}$ is other than a methyl radical, and

wherein color is developed at acidic, neutral or alkaline pH in the presence of at least one oxidizing agent which is added to the at least one dyeing composition only at the time of application or which is present in an oxidizing composition applied simultaneously or sequentially in a separate manner.

- 33. The process according to claim 32, wherein the keratinous fibers are human keratinous fibers.
- The process according to claim 33, wherein the human keratinous fibers are hair.
- 35. The process according to claim 32, comprising a medium appropriate for dyeing.

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- 36. The process according to claim 34, wherein when R_s or R_8 is a halogen atom, said halogen atom is chosen from chlorine, bromine, iodine and fluorine.
- 37. The process according to claim 32, wherein said at least one oxidizing agent is chosen from hydrogen peroxide, urea hydrogen peroxide, alkali metal bromates, persalts, peracids and enzymes.
- 38. A multi-compartment kit device comprising a first compartment and a second compartment, wherein

said first compartment contains a dye composition comprising:

- at least one first oxidation base chosen from pyrazolo(1,5-a)pyrimidines of formula (I) and acid or base addition salts thereof:

$$(X)_{i} = \begin{bmatrix} X_{i} & X_{i} & X_{i} \\ X_{i} & X_{i} & X_{i} \end{bmatrix}_{i} \begin{bmatrix} X_{i} & X_{i} \\ X_{i} & X_{i} \end{bmatrix}_{i}$$

$$(OH)_{n} = \begin{bmatrix} X_{i} & X_{i} \\ X_{i} & X_{i} \end{bmatrix}_{i}$$

$$[NR_{3}R_{4}]_{q}$$

$$(I)$$

in which:

R₁, R₂, R₃ and R₄, which are identical or different, are chosen from a hydrogen atom; a (C₁-C₄)alkyl radical; an aryl radical; a hydroxy(C₁-C₄)alkyl radical; a

$$\label{eq:continuous} \begin{split} &\text{polyhydroxy}(C_2\text{-}C_4)\text{alkyl radical}; \text{ a}(C_1\text{-}C_4)\text{alkoy}(C_1\text{-}C_4)\text{alkyl radical}; \text{ an} \\ &\text{amino}(C_1\text{-}C_4)\text{alkyl radical} \text{ wherein said amine is optionally protected by an acetyl,} \\ &\text{an amido, or a sulphonyl group; a}(C_1\text{-}C_4)\text{alkylamino}(C_1\text{-}C_4)\text{alkyl radical}; \text{ a} \\ &\text{di}((C_1\text{-}C_4)\text{alkyl})\text{amino}(C_1\text{-}C_4)\text{alkyl radical} \text{ wherein said dialkyls optionally form a 5-or 6-membered aliphatic or heterocyclic ring; a} \\ &\text{hydroxy}(C_1\text{-}C_4)\text{alkylamino}(C_1\text{-}C_4)\text{alkyl radical}; \text{ and a} \\ &\text{di}(\text{hydroxy}(C_1\text{-}C_4)\text{alkyl})\text{amino}(C_1\text{-}C_4)\text{alkyl radical}; \end{aligned}$$

- the X radicals, which are identical or different, are chosen from a hydrogen atom; a $(C_1\text{-}C_4)$ alkyl radical; an aryl radical; a hydroxy $(C_1\text{-}C_4)$ alkyl radical; a polyhydroxy $(C_2\text{-}C_4)$ alkyl radical; an amino $(C_1\text{-}C_4)$ alkyl radical; a $(C_1\text{-}C_4)$ alkylamino $(C_1\text{-}C_4)$ alkyl radical; a di $((C_1\text{-}C_4)$ alkyl)amino $(C_1\text{-}C_4)$ alkyl radical wherein said dialkyls optionally form a 5- or 6-membered aliphatic or heterocyclic ring; a hydroxy $(C_1\text{-}C_4)$ alkylamino $(C_1\text{-}C_4)$ alkyl radical; a di $((\text{hydroxy}(C_1\text{-}C_4)$ alkyl)amino $(C_1\text{-}C_4)$ alkyl radical; an amino radical; a $(C_1\text{-}C_4)$ alkylamino radical; a di $((C_1\text{-}C_4)$ alkyl)amino radical; a halogen atom; a carboxylic acid group; and a sulphonic acid group;

- i is 0, 1, 2 and 3;
- p is 0 or 1;
- q is 0 or 1;
- n is 0 or 1:

with the proviso that:

- -(vii) the sum p + q is other than 0;
- -(viii) when p + q is equal to 2, then n is 0 and the NR_1R_2 and NR_3R_4 groups occupy the (2,3), (5,6), (6,7), (3,5) or (3,7) positions;
- -(ix) when p + q is equal to 1, then n is 1 and either the NR_1R_2 or the NR_3R_4 group and the OH group occupy the (2,3), (5,6), (6,7), (3,5) or (3,7) positions;
- at least one second oxidation base chosen from N,N-bis(β -hydroxyethyl)- paraphenylenediamine and its acid addition salts; and
- at least one coupler chosen from meta-phenylenediamines and meta-aminophenols of formula (II) and acid addition salts thereof:

$$\begin{array}{c} \mathsf{R_8} & \mathsf{OH} \\ \mathsf{NHR_6} \end{array} \tag{II)}$$

in which:

- R₅ and R₈, which are identical or different, are chosen from a hydrogen atom, a halogen atom, or a (C₁-C₄)alkyl, monohydroxy(C₁-C₄)alkyl, polyhydroxy(C₂-C₄)alkyl, (C₁-C₄)alkoxy, monohydroxy(C₁-C₄)alkoxy or polyhydroxy(C₂-C₄)alkoxy radical;
- R₆ is chosen from a hydrogen atom and a (C₁-C₄)alkyl, monohydroxy(C₁-C₄)alkyl, polyhydroxy(C₂-C₄)alkyl or an amino(C₁-C₄)alkyl radical;
- R₇ is chosen from a hydrogen atom, a (C₁-C₄)alkyl or (C₁-C₄)alkoxy radical and a halogen atom chosen from chlorine, bromine or fluorine;

it being understood that, when $R_{\rm s}$ represents a chlorine atom and when $R_{\rm s}$ and $R_{\rm 7}$ simultaneously represent a hydrogen atom, then $R_{\rm s}$ is other than a methyl radical, and

- said second compartment contains an oxidizing composition.
- 39. The kit according to claim 38, wherein the at least one dyeing composition further comprises a medium appropriate for dyeing.
- 40. The kit according to claim 38, wherein when $R_{\rm 5}$ or $R_{\rm 8}$ is a halogen atom, said halogen atom is chosen from chlorine, bromine, iodine or fluorine.—

REMARKS

Claims 16-40 are pending. In claim 16, which replaces claim 1, "ureido" has been replaced with "amido" to correct an obvious error as discussed below. As for the remaining claims, support for these claims can be found in the original specification and claims. No new matter has been added. Applicants now await an action on the merits.

Applicants note that they have corrected an obvious error in the claims. Claim 1, at line 17, recites that R_1 , R_2 , R_3 and R_4 each independently can be a C_1 - C_4 aminoalkyl radical wherein the amine may be protected with an "ureido" group. This description is not entirely correct because the amine of the aminoalkyl radical is actually protected <u>as</u> a ureido group, rather than <u>with</u> a ureido group.

A ureido group has the formula -NHCONH $_2$. When R $_2$, for example, represents a C_1 - C_4 aminoalkyl radical wherein the amine is protected as a ureido group, the protected amine corresponds to the following formula: -NR $_1$ - C_1 - C_4 Alk-NHCONH $_2$. Thus, the amine of the C_1 - C_4 aminoalkyl radical is protected with an amido group, i.e., -CONH $_2$, and the protected group corresponds to a ureido radical, i.e, -NHCONH $_2$.

Accordingly, Applicants intend to correct the present specification and have corrected this obvious error in claim 16 (replaces claim 1), in claim 32 (replaces claim 14), and in claim 38 (replaces claim 15). The skilled artisan would have realized that the terminology "protected with a ureido group" should have been recited "protected as an ureido group," or alternatively "protected with an amido group." In order to remain

consistent with the "protected with" language recited in the specification and claims,

Applicants have replaced "ureido" with "amido." Because one of ordinary skill in the art

would have realized the existence of this error in claim 1 and specification, along with

the appropriate correction, the provisos in new claims 16, 32 and 38 regarding the

"amido" group do not constitute new matter. See M.P.E.P. § 2163.07.

Prompt and favorable examination on the merits is respectfully requested.

Please grant any extensions of time required to enter this Preliminary

Amendment and charge any additional required fees to our deposit account 06-0916.

Respectfully submitted,

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COMPOSITION FOR THE OXIDATION DYEING OF KERATINOUS FIBRES AND DYEING PROCESS EMPLOYING THIS COMPOSITION

A subject-matter of the invention is a composition for the oxidation dyeing of keratinous 5 fibres and in particular of human keratinous fibres, such as hair, comprising, in a medium appropriate for dyeing, at least one first oxidation base chosen from pyrazolo[1,5-a]pyrimidines, N,N-bis(β-hydroxyethyl)-para-phenylenediamine as second oxidation base and at 10 least one coupler chosen from meta-aminophenols and meta-phenylenediamines, and the dyeing process employing this composition.

It is known to dye keratinous fibres and in particular human hair with dyeing compositions

15 comprising oxidation dye precursors, in particular ortho- or para-phenylenediamines, ortho- or para-aminophenols or heterocyclic bases, generally known as oxidation bases. Oxidation dye precursors or oxidation bases are colourless or weakly coloured compounds

20 which, in combination with oxidizing substances, can give rise by an oxidative coupling process to coloured and colouring compounds.

It is also known that the shades obtained with these oxidation bases can be varied by combining them with couplers or colouring modifiers, the latter being chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds.

The variety of the molecules employed as Oxidation bases and couplers makes it possible to obtain a rich palette of colours.

The so-called "permanent" colouring obtained

5 by virtue of these oxidation dyes has, however, to
satisfy a certain number of requirements. Thus, it must
make it possible to obtain shades with the desired
intensity and behave well in the face of external
agents (light, bad weather, washing, permanent waving,

10 perspiration or rubbing).

The dyes must also make it possible to cover white hair and, finally, be as unselective as possible, that is to say make it possible to obtain the least possible differences in colouring along the same

15 keratinous fibre, this being because the latter can be sensitized (i.e. damaged) to a varying degree between its tip and its root.

Provision has already been made, in particular in Patent Application FR-A-2,750,048, for compositions for the oxidation dyeing of keratinous fibres comprising, as oxidation base, pyrazolo[1,5-a]-pyrimidines, optionally in combination with one or more couplers. However, the colourings obtained are not always powerful enough, chromatic enough or sufficiently resistant to the various attacks which hair may be subjected to.

In point of fact, the Applicant Company has now just discovered that it is possible to obtain novel

dyes, which dyes are capable of resulting in powerful colourings which are not very selective and which are highly resistant to the various attacks which the fibres may be subjected to, by combining at least one 5 pyrazolo[1,5-a]pyrimidine of formula (I) defined hereinbelow, as first oxidation base, N,N - bis (ß-hydroxyethyl) - para-phenylenediamine and/or at least one of its addition salts with an acid, as second oxidation base, and at least one coupler chosen from suitably selected meta-aminophenols and from meta-phenylenediamines.

This discovery forms the basis of the present invention.

A first subject-matter of the invention is
therefore a composition for the oxidation dyeing of
keratinous fibres and in particular of human keratinous
fibres, such as hair, characterized in that it
comprises, in a medium appropriate for dyeing:
- at least one first oxidation base chosen from
pyrazolo[1,5-a]pyrimidines of following formula (I) or
their addition salts with an acid or with a base:

$$(X)_{i} = \underbrace{\begin{bmatrix} X \\ i \end{bmatrix}}_{5} \underbrace{\begin{bmatrix} X \\ N \\ N \end{bmatrix}}_{2}^{2} \underbrace{\begin{bmatrix} [NR_{1}R_{2}]_{p} \\ [NR_{3}R_{4}]_{q} \end{bmatrix}}_{[NR_{3}R_{4}]_{q}}$$

in which:

- R_1 , R_2 , R_3 and R_4 , which are identical or different, denote a hydrogen atom, a (C_1-C_4) alkyl radical, an aryl radical, a hydroxy (C_1-C_4) alkyl radical, a polyhydroxy (C_2-C_4) alkyl radical, a (C_1-C_4) alkoxy (C_1-C_4) alkyl radical, a (C_1-C_4) alkoxy (C_1-C_4) alkyl radical, a
- 5 alkyl radical, an amino (C_1-C_4) alkyl radical (it being possible for the amine to be protected by an acetyl, a ureido or a sulphonyl), a (C_1-C_4) alkylamino (C_1-C_4) alkyl radical, a di[(C_1-C_4) alkyl] amino (C_1-C_4) alkyl radical (it being possible for the dialkyls to form a 5- or
- 10 6-membered aliphatic or heterocyclic ring), a $\label{eq:hydroxy} hydroxy(C_1-C_4) alkylamino(C_1-C_4) alkyl radical or a \\ di[hydroxy(C_1-C_4) alkyl]amino(C_1-C_4) alkyl radical;$
 - the X radicals, which are identical or different, denote a hydrogen atom, a $(C_1-C_4)\, alkyl$ radical, an aryl
- radical, a hydroxy(C₁-C₄)alkyl radical, a polyhydroxy(C₂-C₄)alkyl radical, an amino(C₁-C₄)alkyl radical, a (C₁-C₄)alkylamino(C₁-C₄)alkyl radical, a di[(C₁-C₄)alkyl]amino(C₁-C₄)alkyl radical (it being possible for the dialkyls to form a 5- or 6-membered
- aliphatic or heterocyclic ring), a $\begin{array}{l} \text{hydroxy}\,(C_1\text{-}C_4)\,\text{alkylamino}\,(C_1\text{-}C_4)\,\text{alkyl radical, a} \\ \\ \text{di}\,[\text{h$^\circ$droxy}\,(C_1\text{-}C_4)\,\text{alkyl}]\,\text{amino}\,(C_1\text{-}C_4)\,\text{alkyl radical, an} \\ \\ \text{amino radical, a}\,\,(C_1\text{-}C_4)\,\text{alkylamino radical, a} \\ \\ \text{di}\,[(C_1\text{-}C_4)\,\text{alkyl}]\,\text{amino radical, a halogen atom, a} \end{array}$
- 25 carboxylic acid group or a sulphonic acid group;
 - i has the value 0, 1, 2 or 3;
 - p has the value 0 or 1;
 - q has the value 0 or 1;

- n has the value 0 or 1; with the proviso that:
- -(i) the sum p + q is other than 0;
- -(ii) when p + q is equal to 2, then n has the value 0 and the NR_1R_2 and NR_3R_4 groups occupy the (2,3), (5,6), (6,7), (3,5) or (3,7) positions:
 - -(iii) when p + q is equal to 1, then n has the value 1 and the NR_1R_2 (or NR_3R_4) group and the OH group occupy the (2,3), (5,6), (6,7), (3,5) or (3,7) positions;
- 10 at least one second oxidation base chosen from $N,N\text{-bis}(\beta\text{-hydroxyethyl})\text{- para-phenylenediamine and}$ its addition salts with an acid; and
- at least one coupler chosen from metaphenylenediamines and meta-aminophenols of following formula (II) and their addition salts with an acid:

in which:

- R₅ and R₈, which are identical or different, represent a hydrogen atom, a halogen atom, such as chlorine, bromine, iodine or fluorine, or a (C₁-C₄)alkyl, monohydroxy(C₁-C₄)alkyl, polyhydroxy(C₂-C₄)alkyl, (C₁-C₄)alkoxy, monohydroxy(C₁-C₄)alkoxy or polyhydroxy(C₂-C₄)alkoxy radical: 10

- R₆ represents a hydrogen atom or a (C₁-C₄)alkyl, monohydroxy (C_1-C_4) alkyl, polyhydroxy (C_2-C_4) alkyl or amino(C1-C4)alkyl radical:
- R7 represents a hydrogen atom, a (C1-C4) alkyl or (C_1-C_4) alkoxy radical or a halogen atom chosen from chlorine, bromine or fluorine;

it being understood that, when R_{S} represents a chlorine atom and when R_6 and R_7 simultaneously represent a hydrogen atom, then R_{θ} is other than a methyl radical.

The dyeing composition in accordance with the invention results in powerful and chromatic colourings which exhibit low selectivity and excellent properties of resistance both with respect to atmospheric agents, such as light and bad weather, and with respect to 15 perspiration and various treatments which hair may be subjected to.

Another subject-matter of the invention is a process for the oxidation dyeing of keratinous fibres employing this dyeing composition.

20 The pyrazolo[1,5-a]pyrimidines of formula (I) which can be used as first oxidation base in the dyeing composition in accordance with the invention are known compounds which are disclosed in Patent Application FR-A-2,750,048, the contents of which form an integral 25 part of the present application.

Mention may in particular be made, among the pyrazolo[1,5-a]pyrimidines of formula (I) which can be used as oxidation base in the dyeing compositions in accordance with the invention. of:

- pyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 2-methylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 5 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
 - pyrazolo[1,5-a]pyrimidine-3,5-diamine;
 - 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine;
 - 3-aminopyrazolo[1,5-a]pyrimidin-7-ol;
 - 3-amino-5-methylpyrazolo[1,5-a]pyrimidin-7-ol;
- 10 3-aminopyrazolo[1,5-a]pyrimidin-5-ol;
 - 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol;
 - 3-amino-7-(β-hydroxyethylamino)-5-methylpyrazolo-[1,5-a]pyrimidine;
 - 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol;
- 15 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl) (2-hydroxyethyl)amino]ethanol;
 - 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)(2-hydroxyethyl)aminolethanol:
 - 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 20 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine:
 - 2,5,N-7,N-7-tetramethylpyrazolo[1,5-a] pyrimidine-3,7diamine;

and their addition salts with an acid or with a base.

The meta-phenylenediamines which can be used

25 as coupler in the dyeing composition in accordance with the invention are preferably chosen from the compounds of following formula (III) and their addition salts with an acid:

in which:

- R_9 represents a hydrogen atom or a (C_1-C_4) alkyl, monohydroxy (C_2-C_4) alkyl or polyhydroxy (C_2-C_4) alkyl
- 5 radical;
 - R_{10} and R_{11} , which are identical or different, represent a hydrogen atom or a (C_1-C_4) alkyl, monohydroxy (C_1-C_4) alkoxy or polyhydroxy (C_2-C_4) alkoxy radical;
- 10 R₁₂ represents a hydrogen atom, a (C₁-C₄)alkoxy, amino(C₁-C₄)alkoxy, monohydroxy(C₁-C₄)alkoxy or polyhydroxy(C₂-C₄)alkoxy radical or a 2,4-diaminophenoxyalkoxy radical.
- Mention may more particularly be made, among 15 the meta-phenylenediamines of formula (III) above, of
- meta-phenylenediamine, 3,5-diamino-1-ethyl-2-methoxybenzene, 3,5-diamino-2-methoxy-1-methylbenzene,
 - 2,4-diamino-1-ethoxybenzene, 1,3-bis(2,4-diamino-phenoxy) propane, bis(2,4-diaminophenoxy) methane,
- 20 1-(β -aminoethyloxy)-2,4-diaminobenzene, 2-amino-
 - 1-(β-hydroxyethyloxy)-4-(methylamino)benzene,
 - 2,4-diamino-1-ethoxy-5-methylbenzene, 2,4-diamino-5-
 - $(\beta-hydroxyethyloxy)-1-methylbenzene, 2,4-diamino-$

1- $(\beta, \gamma$ -dihydroxypropyloxy) benzene, 2,4-diamino-1- $(\beta$ -hydroxyethyloxy) benzene, 2-amino-4-N- $(\beta$ -hydroxyethyl) amino-1-methoxybenzene and their addition salts with an acid.

- 5 Mention may more particularly be made, among the meta-aminophenols of formula (II) which can be used as coupler in the dyeing composition in accordance with the invention, of meta-aminophenol, 5-amino-2-methoxyphenol, 5-amino-2-(β-hydroxyethyloxy)phenol, 10 5-amino-2-methylphenol, 5-N-(β-hydroxyethyl)amino-2-methylphenol, 5-N-(β-hydroxyethyl)amino-4-methoxy-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-6-methoxyphenol, 3-amino-6-chlorophenol, 3-amino-6-chlor
 - 6 2-methylphenol, 3-amino-b-chlorophenol, 3-(β-amino-b-chlorophenol,
 3-(β-hydroxyethyl)amino-b-chlorophenol and their
 addition salts with an acid.

The pyrazolo[1,5-a]pyrimidine or

- pyrazolo[1,5-a]pyrimidines of formula (I) in accordance
 with the invention and/or the addition salt or their
 addition salts with an acid or with a base preferably
 represent from 0.0005 to 12% by weight approximately of
 the total weight of the dyeing composition in
- 25 accordance with the invention and more preferably still from 0.005 to 6% by weight approximately of this weight.

N,N -Bis(β-hydroxyethyl) - para-phenylenediamine and/or the addition salt or its addition salts with an acid which can be used as second oxidation base in the dyeing composition in accordance with the 5 invention preferably represent from 0.0005 to 12% by weight approximately of the total weight of the dyeing composition in accordance with the invention and more preferably still from 0.005 to 6% by weight approximately of this weight.

The meta-phenylenediamine or metaphenylenediamines and/or the meta-aminophenol or metaaminophenols of formula (II) and/or the addition salt
or their addition salts with an acid preferably
represent from 0.0001 to 10% by weight approximately of
the total weight of the dyeing composition and more
preferably still from 0.005 to 5% by weight
approximately of this weight.

The dyeing composition in accordance with the invention can additionally comprise one or more

20 couplers other than the meta-phenylenediamines and the meta-aminophenols of formula (II) and/or one or more direct dyes, in particular for modifying the shades or enriching them with highlights.

Mention may in particular be made, among the

couplers which can additionally be present in the

dyeing composition according to the invention, of metadiphenols, heterocyclic couplers and their addition

salts with an acid.

Generally, the addition salts with an acid
which can be used in the context of the dyeing
compositions of the invention (oxidation bases and
couplers) are chosen in particular from hydrochlorides,
hydrobromides and sulphates and tartrates, lactates and
acetates. The addition salts with a base which can be
used in the context of the dyeing compositions of the
invention are in particular those obtained with sodium
hydroxide, potassium hydroxide, aqueous ammonia or

The medium appropriate for dyeing (or vehicle) of the dyeing composition in accordance with the invention is generally composed of water or of a mixture of water and of at least one organic solvent,

15 in order to dissolve the compounds which would not be sufficiently soluble in water. Mention may be made, for example, as organic solvent, of C₁-C₄ alkanols, such as ethanol and isopropanol; glycerol; glycols and glycol ethers, such as 2-butoxyethanol, propylene glycol,

20 propylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monomethyl ether; and aromatic alcohols, such as benzyl alcohol or phenoxyethanol, the analogous products and their mixtures.

25 The solvents can be present in proportions preferably of between 1 and 40% by weight approximately with respect to the total weight of the dyeing composition and more preferably still between 5 and 30% by weight approximately.

The pH of the dyeing composition in accordance with the invention is generally between 3 and 12 approximately and preferably between 5 and 12 approximately. It can be adjusted to the desired value by means of acidifying or basifying agents commonly used in dyeing keratinous fibres.

Mention may be made, among acidifying agents,

10 by way of example, of inorganic or organic acids, such
as hydrochloric acid, orthophosphoric acid, sulphuric
acid, carboxylic acids, such as acetic acid, tartaric
acid, citric acid or lactic acid, or sulphonic acids.

Mention may be made, among basifying agents,

15 by way of example, of aqueous ammonia, alkaline
carbonates, alkanolamines, such as mono-, di- and
triethanolamines, 2-methyl-2-aminopropanol and their
derivatives, sodium hydroxide, potassium hydroxide and
the compounds of following formula (IV):

20

$$R_{13}$$
 N-W-N R_{16} (IV)

in which W is a propylene residue optionally substituted by a hydroxyl group or a (C_1-C_4) alkyl radical and R_{13} , R_{14} , R_{15} and R_{16} , which are identical or different, represent a hydrogen atom or a (C_1-C_4) alkyl or hydroxy (C_1-C_4) alkyl radical.

The dyeing composition in accordance with the invention can also include various adjuvants conventionally used in hair dyeing compositions, such as anionic, cationic, non-ionic, amphoteric or zwitterionic surface-active agents or their mixtures, anionic, cationic, non-ionic, amphoteric or zwitterionic polymers or their mixtures, inorganic or organic thickening agents, such as, for example, non-ionic guar gums, antioxidizing agents, enzymes, such as 2-electron oxidoreductases, peroxidases or laccases, penetration agents, sequestering agents, fragrances, buffers, dispersing agents, conditioning agents, such as, for example, volatile or nonvolatile and modified or unmodified silicones, film-forming agents,

15 ceramides, preserving agents or opacifying agents.

Of course, a person skilled in the art will take care to choose this or these optional additional compound or compounds so that the advantageous properties intrinsically attached to the dyeing

composition in accordance with the invention are not, or not substantially, detrimentally affected by the envisaged addition or additions.

The dyeing composition in accordance with the invention can be provided in various forms, such as in the form of liquids, powders, creams or gels, which are optionally pressurized, or in any other form appropriate for carrying out dyeing of keratinous fibres and in particular human hair.

Another subject-matter of the invention is a process for dyeing keratinous fibres and in particular human keratinous fibres, such as hair, employing the dyeing composition as defined above.

5 According to this process, the dyeing composition as defined above is applied to the fibres, the colour being developed at acidic, neutral or alkaline pH using an oxidizing agent which is added only at the time of use to the dyeing composition or which is present in an oxidizing composition applied simultaneously or sequentially in a separate fashion.

According to a particularly preferred embodiment of the dyeing process according to the invention, the dyeing composition described above is mixed, at the time of use, with an oxidizing composition comprising, in a medium appropriate for dyeing, at least one oxidizing agent present in an amount sufficient to develop a colouring. The mixture obtained is subsequently applied to the keratinous fibres and is left to stand for 3 to 50 minutes approximately, preferably 5 to 30 minutes approximately, after which the hair is rinsed, washed with a shampoo, rinsed again and dried.

The oxidizing agent present in the oxidizing
composition as defined above can be chosen from
oxidizing agents conventionally used for the oxidation
dyeing of keratinous fibres and among which may be
mentioned hydrogen peroxide, urea hydrogen peroxide,

alkali metal bromates, persalts, such as perborates and persulphates, peracids or enzymes, such as 2-electron oxidoreductases, peroxidases and laccases. Hydrogen peroxide is particularly preferred.

The pH of the oxidizing composition including the oxidizing agent as defined above is such that, after mixing with the dyeing composition, the pH of the resulting composition applied to keratinous fibres preferably varies between 3 and 12 approximately and more preferably still between 5 and 11. It is adjusted to the desired value by means of acidifying or basifying agents commonly used in dyeing keratinous fibres and as defined above.

The oxidizing composition as defined above

15 can also include various adjuvants conventionally used
in hair dyeing compositions and as defined above.

The composition which is finally applied to keratinous fibres can be provided in various forms, such as in the form of liquids, creams or gels, or in any other form appropriate for carrying out dyeing of keratinous fibres and in particular of human hair.

- Another subject-matter of the invention is a dyeing multi-compartment device or kit or any other packaging system with several compartments, a first compartment of which includes the dyeing composition as defined above and a second compartment of which includes the oxidizing composition as defined above. These devices can be equipped with a means allowing the

desired mixture to be deposited on the hair, such as the devices disclosed in Patent FR-2,586,913 on behalf of the Applicant Company.

The examples which follow are intended to

5 illustrate the invention without, however, limiting the
scope thereof.

EXAMPLES

DYEING EXAMPLES 1 AND 2

The following dyeing compositions were

10 prepared (contents in grams):

EXAMPLE	1	2
Pyrazolo[1,5-a]pyrimidine-3,7-diamine·2HCl	0.666	0.666
N,N -Bis(β-hydroxyethyl)- para-	0.936	0.936
phenylenediamine		
2-Methyl-5-[N-(β-hydroxyethyl)amino]phenol	1.0	-
2,4-Diamino-1-(β-hydroxyethyloxy)benzene-2HCl	-	1.446
Common dyeing vehicle	(*)	(*)
Demineralized water, q.s. for	100 g	100 g

(*): Common dyeing vehicle:

- 96° Ethyl alcohol

18 q

- Pentasodium salt of diethylenetriaminepentaacetic acid

1.1 g

15 - Aqueous ammonia comprising 20% of NH3

10 g

At the time of use, each of the dyeing compositions described above was mixed, weight for weight, with a 20-volume hydrogen peroxide solution (6% by weight).

Each of the mixtures thus prepared was applied for 30 minutes to locks of natural grey hair comprising 90% of white hairs. The locks were subsequently rinsed, washed with a standard shampoo, 5 rinsed again and then dried.

The hair was dyed in a shade which appears in the table below:

EXAMPLE	SHADE OBTAINED	
1	Deep ash purple	
2	Blue	

CLAIMS

- Composition for the oxidation dyeing of keratinous fibres and in particular of human keratinous fibres, such as hair, characterized in that it
- 5 comprises, in a medium appropriate for dyeing:
 at least one first oxidation base chosen from pyrazolo[1,5-a]pyrimidines of following formula (I) or their addition salts with an acid or with a base:

$$(X)_{i} = \begin{bmatrix} X & X & X \\ X & X & X \end{bmatrix}_{i} \begin{bmatrix} X & X & X \\ X & X & X \end{bmatrix}_{i} \begin{bmatrix} X & X & X \\ X & X & X \end{bmatrix}_{i}$$

$$(OH)_{n} = \begin{bmatrix} X & X & X \\ Y & X & X \end{bmatrix}_{i} \begin{bmatrix} X & X & X \\ Y & X & X \end{bmatrix}_{i}$$

$$(I)$$

10

in which:

- R₁, R₂, R₃ and R₄, which are identical or different, denote a hydrogen atom, a (C₁-C₄) alkyl radical, an aryl radical, a hydroxy(C₁-C₄) alkyl radical, a polyhydroxy(C₂-C₄) alkyl radical, a (C₁-C₄) alkoxy(C₁-C₄) -

- alkyl radical, an amino (C_1-C_4) alkyl radical (it being possible for the amine to be protected by an acetyl, a ureido or a sulphonyl), a (C_1-C_4) alkylamino (C_1-C_4) alkyl radical, a di $\{(C_1-C_4)$ alkyl amino (C_1-C_4) alkyl radical (it
- 20 being possible for the dialkyls to form a 5- or 6-membered aliphatic or heterocyclic ring), a hydroxy(C₁-C₄)alkylamino(C₁-C₄)alkyl radical or a di[hydroxy(C₁-C₄)alkyl]amino(C₁-C₄)alkyl radical;
 - the X radicals, which are identical or different,
- 25 denote a hydrogen atom, a (C_1-C_4) alkyl radical, an aryl

- radical, a hydroxy(C_1 - C_4) alkyl radical, a polyhydroxy(C_2 - C_4) alkyl radical, an amino(C_1 - C_4) alkyl radical, a di[(C_1 - C_4) alkyl] amino(C_1 - C_4) alkyl radical, a di[(C_1 - C_4) alkyl] amino(C_1 - C_4) alkyl radical (it being
- 5 possible for the dialkyls to form a 5- or 6-membered aliphatic or heterocyclic ring), a $\label{eq:hydroxy} hydroxy(C_1-C_4) alkylamino(C_1-C_4) alkyl radical, a \\ \mbox{di}[hydroxy(C_1-C_4) alkyl]amino(C_1-C_4) alkyl radical, an amino radical, a (C_1-C_4) alkylamino radical, a$
- 10 $\text{di}[(C_1-C_4)alkyl]$ amino radical, a halogen atom, a carboxylic acid group or a sulphonic acid group;
 - i has the value 0, 1, 2 or 3;
 - p has the value 0 or 1;
 - q has the value 0 or 1;
- 15 n has the value 0 or 1;
 with the proviso that:
 - -(i) the sum p + q is other than 0;
 - -(ii) when p + q is equal to 2, then n has the value 0 and the NR_1R_2 and NR_3R_4 groups occupy the (2,3), (5,6),
- 20 (6,7), (3,5) or (3,7) positions;
 - -(iii) when p + q is equal to 1, then n has the value 1 and the NR_1R_2 (or NR_3R_4) group and the OH group occupy the (2,3), (5,6), (6,7), (3,5) or (3,7) positions;
 - at least one second oxidation base chosen from
- N,N-bis(β-hydroxyethyl) para-phenylenediamine and its addition salts with an acid; and

- at least one coupler chosen from metaphenylenediamines and meta-aminophenols of following formula (II) and their addition salts with an acid:

$$R_8$$
 NHR_6 (II)

5 in which:

10

- R_S and R_B, which are identical or different, represent a hydrogen atom, a halogen atom, such as chlorine, bromine, iodine or fluorine, or a (C₁-C₄)alkyl, monohydroxy(C₁-C₄)alkyl, polyhydroxy(C₂-C₄)alkyl, (C₁-C₄)alkoxy, monohydroxy(C₁-C₄)alkoxy or polyhydroxy(C₂-C₄)alkoxy radical;
- R_6 represents a hydrogen atom or a (C_1-C_4) alkyl, monohydroxy (C_1-C_4) alkyl, polyhydroxy (C_2-C_4) alkyl or amino (C_1-C_4) alkyl radical;
- 15 R₇ represents a hydrogen atom, a (C₁-C₄) alkyl or (C₁-C₄) alkoxy radical or a halogen atom chosen from chlorine, bromine or fluorine;
 - it being understood that, when R_{S} represents a chlorine atom and when R_{G} and R_{7} simultaneously represent a
- 20 hydrogen atom, then R_8 is other than a methyl radical.
 - 2. Composition according to Claim 1, characterized in that the pyrazolo[1,5-a]pyrimidines of formula (I) are chosen from:
 - pyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 25 2-methylpyrazolo[1,5-a]pyrimidine-3,7-diamine;

- 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- pyrazolo[1,5-a]pyrimidine-3,5-diamine;
- 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine;
- 3-aminopyrazolo[1,5-a]pyrimidin-7-ol;
- 5 3-amino-5-methylpyrazolo[1,5-a]pyrimidin-7-ol;
 - 3-aminopyrazolo[1,5-a]pyrimidin-5-ol;
 - 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol;
 - 3-amino-7-(β-hydroxyethylamino)-5-methylpyrazolo-[1,5-a]pyrimidine;
- 10 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol;
 - 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)(2-hydroxyethyl)amino]ethanol;
 - 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)(2-hydroxyethyl)aminolethanol;
- 15 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
 - 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
 - 2,5,N-7,N-7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7diamine;

and their addition salts with an acid or with a base.

20 3. Composition according to Claim 1 or 2, characterized in that the meta-phenylenediamines are chosen from the compounds of following formula (III) and their addition salts with an acid:

in which:

- R_9 represents a hydrogen atom or a (C_1-C_4) alkyl, monohydroxy (C_2-C_4) alkyl or polyhydroxy (C_2-C_4) alkyl radical:
- 5 R₁₀ and R₁₁, which are identical or different, represent a hydrogen atom or a (C₁-C₄)alkyl, monohydroxy(C₁-C₄)alkoxy or polyhydroxy(C₂-C₄)alkoxy radical;
- R₁₂ represents a hydrogen atom, a (C₁-C₄) alkoxy, 10 amino(C₁-C₄) alkoxy, monohydroxy(C₁-C₄) alkoxy or polyhydroxy(C₂-C₄) alkoxy radical or a 2,4-diaminophenoxyalkoxy radical.
- 4. Composition according to Claim 3, characterized in that the meta-phenylenediamines are 15 chosen from meta-phenylenediamine, 3,5-diamino-1-ethyl-2-methoxybenzene, 3,5-diamino-2-methoxy-1-methylbenzene, 2,4-diamino-1-ethoxybenzene, 1,3-bis(2,4-diaminophenoxy)propane, bis(2,4-diaminophenoxy)methane, 1-(β-aminoethyloxy)-
- 20 2,4-diaminobenzene, 2-amino-1-(β-hydroxyethyloxy)4-(methylamino)benzene, 2,4-diamino-1-ethoxy5-methylbenzene, 2,4-diamino-5-(β-hydroxyethyloxy)1-methylbenzene, 2,4-diamino-1-(β,γ-dihydroxypropyloxy)benzene, 2,4-diamino-1-(β-hydroxyethyloxy)benzene,
- 25 2-amino-4-N- $(\beta$ -hydroxyethyl)amino-1-methoxybenzene and their addition salts with an acid.
 - Composition according to Claim 1 or 2, characterized in that the meta-aminophenols are chosen

- from meta-aminophenol, 5-amino-2-methoxyphenol, 5-amino-
- 2- $(\beta$ -hydroxyethyloxy)phenol, 5-amino-2-methylphenol,
- 5-N-(β-hydroxyethyl) amino-2-methylphenol,
- $5-N-(\beta-hydroxyethyl)$ amino-4-methoxy-2-methylphenol,
- 5 5-amino-4-methoxy-2-methylphenol, 5-amino-4-chloro-
 - 2-methylphenol, 5-amino-2,4-dimethoxyphenol,
 - 5- $(\gamma$ -hydroxypropylamino)-2-methylphenol, 3-amino-
 - 6-chlorophenol, 3-amino-6-bromophenol,
 - 3-(β-aminoethyl)amino-6-chlorophenol,
- 10 3-(β-hydroxyethyl)amino-6-chlorophenol and their addition salts with an acid.
- 6. Composition according to any one of the preceding claims, characterized in that the pyrazolo[1,5-a]pyrimidine or pyrazolo[1,5-a]pyrimidines of formula (I) and/or the addition salt or their addition salts with an acid or with a base represent from 0.0005 to 12% by weight of the total weight of the dveing composition.
 - 7. Composition according to Claim 6,
- 20 characterized in that the pyrazolo[1,5-a]pyrimidine or pyrazolo[1,5-a]pyrimidines of formula (I) and/or the addition salt or their addition salts with an acid or with a base represent from 0.005 to 6% by weight of the total weight of the dyeing composition.
- 25 8. Composition according to any one of the preceding claims, characterized in that N,N -bis(β -hydroxyethyl) para-phenylenediamine and/or the addition salt or its addition salts with an acid

represent from 0.0005 to 12% by weight of the total weight of the dveing composition.

- 9. Composition according to Claim 8, characterized in that N,N -bis(β -hydroxyethyl) para-phenylenediamine and/or the addition salt or its addition salts with an acid represent from 0.005 to 6% by weight of the total weight of the dyeing composition.
- 10. Composition according to any one of the
 10 preceding claims, characterized in that the metaphenylenediamine or meta-phenylenediamines and/or the
 meta-aminophenol or meta-aminophenols of formula (II)
 and/or the addition salt or their addition salts with
 an acid represent from 0.0001 to 10% by weight of the
 15 total weight of the dyeing composition.
- 11. Composition according to Claim 10, characterized in that the meta-phenylenediamine or meta-phenylenediamines and/or the meta-aminophenol or meta-aminophenols of formula (II) and/or the addition 20 salt or their addition salts with an acid represent from 0.005 to 5% by weight of the total weight of the dyeing composition.
- 12. Composition according to any one of the preceding claims, characterized in that the addition
 25 salts with an acid are chosen from hydrochlorides, hydrobromides and sulphates and tartrates, lactates and acetates and in that the addition salts with a base are

chosen from those obtained with sodium hydroxide, potassium hydroxide, aqueous ammonia or amines.

- 13. Process for dyeing keratinous fibres and in particular human keratinous fibres, such as hair,
 5 characterized in that at least one dyeing composition as defined in any one of Claims 1 to 12 is applied to the said fibres and in that the colour is developed at acidic, neutral or alkaline pH using an oxidizing agent which is added only at the time of use to the dyeing composition or which is present in an oxidizing composition applied simultaneously or sequentially in a separate fashion.
- 14. Process according to Claim 13, characterized in that the oxidizing agent present in the oxidizing composition is chosen from hydrogen peroxide, urea hydrogen peroxide, alkali metal bromates, persalts, peracids and enzymes.
- 15. Dyeing multi-compartment device or kit with several compartments, a first compartment of which includes a dyeing composition as defined in any one of Claims 1 to 12 and a second compartment of which includes an oxidizing composition.

ABSTRACT

COMPOSITION FOR THE OXIDATION DYEING OF KERATINOUS FIBRES AND DYEING PROCESS EMPLOYING THIS COMPOSITION

A subject-matter of the invention is a composition for the oxidation dyeing of keratinous fibres and in particular of human keratinous fibres, such as hair, comprising, in a medium appropriate for dyeing, at least one first oxidation base chosen from pyrazolo[1,5-a]pyrimidines, N,N-bis(β -hydroxyethyl)-para-phenylenediamine as second oxidation base and at least one coupler chosen from meta-aminophenols and meta-phenylenediamines, and the dyeing process employing this composition.

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Declaration and Power of Attorney for Patent Application Déclaration et Pouvoir pour Demand de Brevet

En tant que l'inventeur nommé ci-après, je déclare par le présent As a below named inventor, I hereby declare that:

acte que:

French Language Declaration

Mon domicile, mon adresse postale et ma nationalité sont ceux figurant ci-dessous à côté de mon nom.	My residence, post office address and citizenship are as stated next to my name.
le crois être le premier inventeur original et unique (si un seul nom est mentionné ci-dessous), ou l'un des premiers co-inventeurs originaux (si plusieurs noms sont mentionnés ci-dessous) de l'objet revendiqué, pour lequel une demande de bevet a été déposée concernant l'invention intitulée	I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled
	OXIDATION DYEING COMPOSITION FOR KERATINOUS FIBRES AND DYEING METHOD USING SAME
gradit dont la description est fournie ci-joint à moins que la case suivante n'ait été cochée:	the specification of which is attached hereto unless the following box is checked:
a été déposée le	awas filed on June 2, 1999 as United States Application Number or PCT International Application Number PCT/FR99/01291 and was amended on (if applicable).
le déclare par le présent acte avoir passé en revue et compris le contenu de la description ci-dessus, revendications comprises, elles que modifées par toute modification dont il aura été fait éférence ci-dessus.	I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above
le reconnais devoir divulguer toute information pertinente à la prevetabilité, comme défini dans le Titre 37, § 1.56 du Code rédéral des réglementations.	I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

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19 June 1998 (Day/Month/Year Filed) (Jour/Mois/Anné de dépot) (Day/Month/Year Filed)

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Je revendique par le présent acte avoir la priorité étrangère, en vertu di Titre 35, § 119(a)-(d) ou § 365(b) du Code des Etats-Unis, sur toute demande étrangère de brevet ou certificat d'inventeur ou, en vertu du Titre 35, § 365(a) du même Code, sur toute demande internationale PCT désignant au moins un pays autre que les Etats-Unis et fligurant ci-dessous et, en cochant la case, j'ai aussi indiquéci-dessous foute demande étrangère de brevet, tout certificat d'inventeur ou toute demande internationale PCT ayant une date de dépôt précédant celle de la demande à propos de laquelle une priorité est revendiouée.

I hereby claim foreign priority under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International Application which designated at least one country other than the United States, listed below, and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Prior foreign application(s)
Demande(s) de brevet antérieure(s)

98/07794 (Number) (Numéro)	(Country) (Pays)
(Number)	(Country)
(Numéro)	(Pays)

Priority Not Claimed Droit de priorité non revendiqué

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(Application No.)	(Filing Date)
(No de demande)	(Date de dépot)
(Application No.)	(Filing Date)
(N ⁰ de demande)	(Date de dépot)

(Joúr/Mois/Anné de dépot)

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I hereby claim the benefit under Title 35, United States Code, \$120 of any United States application(s), or § 365(o) of any PCT International Application designating the United States, listed the property of the supplication is not disclosed in the prior United States, listed this application is not disclosed in the prior United States or PCT International Application in the manner provided by the first paragraph of Title 35, United States Code, § 11.2, lacknowledge the duty to disclose any or all information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(Application No.)	(Filing Date)
(N ⁰ de demande)	(Date de dépot)
(Application No.)	(Filing Date)
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(Status) (patented, pending, abandoned) (Status) (breveté, en cours d'examen, abandonné) (Status) (patented, pending, abandoned) (Status) (breveté, en cours d'examen, abandonné)

Je déclare par le présent acte que toute déclaration ci-incluse est, à ma connaissance, véridique et que toute déclaration formulée à partir de renseignements ou de suppositions est tenue pour véridique; et de plus, que toutes ces déclarations ont été formulées en sachant que toute fausse déclaration volontaire ou son équivalent est passible d'une amende ou d'une incarcération, ou des deux, en vertu de la Section 1001 du Titre 18 du Code des États-Unis, et que de telte déclarations volontairement fausses risquent de compromettre la validité de la demande de brevet ou du brevet délivré à partir de celleI hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willfulf lake statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willfulf alse statements may jeopardize the validity of the application or any patent issued thereon.

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POUVOIRS: En tant que l'inventeur cité, je désigne par la présente l'(les) avocat(s) et/ou agent(s) suivant(s) pour qu'ils poursuive(nt) la procédure de cette demande de brevet et traite(nt) toute affaire s'y rapportant avec L'Office des brevets et des marques: (mentionner le nom et le numéro d'enregistrement).



POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this patent application and transcat all business in the Patent and Trademark Office connected therewith: (list name and registration number):

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